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13. ABSTRACT (Maximum 200 words) The time-dependent decrease in ortho-positronium (o-Ps) intensity detected in polymers during long-term positron annihilation lifetime (PALS) experiments has been extensively studied and modeled. This decrease is temperature dependent, polymer specific, source strength dependent and is noted to saturate as a function of source exposure time. Larger decreases and smaller saturation values are exhibited at lower temperatures. Additionally, at sufficiently high temperatures, a negligible decrease is detected. The time dependent decrease is recoverable at elevated temperatures. In contrast, the o-Ps lifetime component remains constant and independent of exposure time. Increasing the exposed sample volume by continuously varying the source-sample orientation dramatically decreases the reduction of o-Ps intensity.				
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PROBLEM STUDIED

Positron annihilation lifetime spectroscopy (PALS) was used to obtain isothermal data for thermotropic liquid crystalline/thermoplastic composites. The composites were a blend of polypropylene and the TLCP Vectra (an aromatic copolyester of 73% hydrobenzoic acid and 27% 2-hydroxy 6-naphtholic acid). The injection molded melt blended composites were processed over a year prior to PALS measurements in order to eliminate possible aging effects. In addition to pure polypropylene Vectra samples, blends of 70, 80, 90, and 96 weight percent polypropylene were also investigated. Isothermal data collected at 20°C revealed that the ortho-positronium (o-Ps) lifetime (t_3) remained constant and independent of source exposure. In contrast, the o-Ps intensity (I_3) decreased with increased source exposure time. The pure Vectra sample did not exhibit a time-dependent decrease in I_3 .

Assuming that the composites had reached a state of structural equilibrium, which is a valid assumption given that they were molded well over a year prior to PALS measurements, the o-Ps lifetime and intensity values should remain constant as a function of time at constant temperature. Therefore, a constant lifetime coupled with a decreasing intensity value suggests that the size of the free volume cavity sites are remaining constant but their concentration is decreasing. An alternative explanation is that the size of the free volume cavity sites are constant and the formation probability o-Ps, not the free volume concentration, is decreasing. This decrease, or inhibition, is believed to be the result of prolonged positron source exposure.

Given that the time-dependent decrease in o-Ps intensity was exhibited in the samples containing polypropylene but not in the pure Vectra sample, and that the magnitude of the observed inhibition was proportional to the PP content, a comprehensive study of the positron irradiation effect in polypropylene was performed.

SUMMARY OF RESULTS

The following are the major experimental results observed regarding the positron irradiation effects observed during long-term positron annihilation experiments in polymers.

1. ^{22}Na positron source irradiation causes time-dependent inhibition of both ortho- and para-positronium in isotactic polypropylene, atactic polystyrene and polytetrafluoroethylene.
2. The positron source irradiation effect is not observed in polycarbonate, poly(vinyl chloride), Ultem (polyetherimide), and Vectra.
3. The ortho-positronium intensity decrease in isotactic polypropylene is stable at room temperature upon removal of the positron source for at least 700 hours (30 days).
4. The magnitude of the o-Ps intensity decrease is temperature dependent in isotactic polypropylene. Larger decreases are observed at lower temperature between -30 and 100°C.
5. The positron irradiation effect is negligible at 100°C in isotactic polypropylene.
6. The positron irradiation effect accumulated at room temperature is completely recoverable upon annealing for 10 hours at 100°C.
7. The time dependent o-Ps intensity decrease caused by positron source exposure saturates at a value which is temperature dependent. Higher saturation values are observed at higher temperatures over the range -30 to 100°C.
8. The positron irradiation effect in isotactic polypropylene is not dependent on irradiation environment. Similar positronium inhibition is observed when irradiated in air, vacuum, and flowing argon.

9. The o-Ps lifetime component can be correlated with the increase in molecular free volume caused by increased temperature in isotactic polypropylene.

These experimental findings have led to the following conclusions.

1. The o-Ps intensity component in polymers cannot always be interpreted solely as a measure of free volume site concentration. The influence of polymer chemistry on positronium formation must also be considered.

2. The PALS technique cannot be strictly considered a non-destructive technique.

3. The positronium inhibition observed in atactic polystyrene is not indicative of physical aging.

4. The positron irradiation effect can be significantly reduced by limiting source exposure through continually varying source-sample orientation. As a result, the PALS technique can still be used to detect physical aging effects in polymers.

5. The positron irradiation effect in isotactic polypropylene is most likely not caused by spin conversion. This conclusion is based on the low probability of para-to-ortho positronium conversion.

6. The irradiation effect in PP is most likely not caused by radiation induced crosslinking or main chain scission. The major failing of this explanation is that crosslinking and main-chain scission are permanent structural changes.

7. The irradiation effect in PP is most likely not caused by the methyl group rotation inhibition mechanism. The methyl end groups are formed as a result of main chain scission and therefore this mechanism cannot explain the observed temperature recovery of the irradiation effect.

8. The irradiation effect in isotactic polypropylene is most likely not caused by inhibiting effects of carbonyl groups.

9. The irradiation effect in PP is most likely not caused by a locally generated electric field. Only 4.1×10^{-8} percent of the available electrons in the irradiated PP volume are depleted after 60 hours of continuous exposure to a 20 micro-curie ^{22}Na source.

10. The irradiation effect in PP is most likely not caused by free volume exclusion due to hydrogen adsorption. This conclusion is based on the fact that the adsorption of a monolayer of hydrogen does not reduce the available free volume below the level necessary for positronium formation.

11. The irradiation effect is most likely the result of positronium inhibition. Positronium inhibition is consistent with the observed decrease in both para and ortho-positronium intensity. The proposed inhibition mechanism is free electron scavenging by primary polypropylene free radicals. Positron scavenging is unlikely given the non-polar nature of isotactic polypropylene. The time dependent behavior of the positron irradiation effect is consistent with increased radical concentration. Furthermore, the stability of the positron irradiation effect is consistent with trapped polypropylene free radicals. The temperature dependence of the positron irradiation effect is consistent with the dependence of free radical concentration on temperature. Similarly, the negligible positron irradiation effect at 100°C and the temperature recovery following an anneal at 100°C are consistent with termination of the majority of free radicals. Finally, the saturation of the positron irradiation effect is consistent with a fraction of free electrons which do

not thermalize in the vicinity of a trapped free radical and therefore escape combination and contribute to positronium formation.

12. The polymer specificity of the positron irradiation effect is possibly correlated with the presence of local dipoles. These dipoles provide the epithermal positrons and electrons with an additional mechanism through which to lose their excess energy. Consequently, the mean positron-electron thermalization distance is decreased. In addition, the mean positron-electron thermalization distance is dependent on polymer density, with higher densities leading to smaller mean thermalization distances. It is possible that the decreased mean positron-electron thermalization distance reduces the efficiency of the free radical scavengers. Therefore, a correlation between the positron irradiation effect and the polymer polarity and density is suggested.

13. Epithermal positronium reaction with trapped polypropylene free radicals is also consistent with the observed positron irradiation effect.

PUBLICATIONS

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